

Evidence of a critical hole concentration in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_y$ single crystals revealed by ^{63}Cu NMR

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We report a ^{63}Cu NMR investigation in detwinned $\text{YBa}_2\text{Cu}_3\text{O}_y$ single crystals, focusing on the highly underdoped regime ($y = 6.35$ – 6.6). Measurements of both the spectra and the spin-lattice relaxation rates of ^{63}Cu uncover the emergence of static order at a well-defined onset temperature T_0 without a known order parameter as yet. While T_0 is rapidly suppressed with increasing hole doping concentration p , the spin pseudogap was identified only near and above the doping content at which $T_0 \rightarrow 0$. Our data indicate the presence of a critical hole doping $p_c \sim 0.1$, which may control both the static order at $p < p_c$ and the spin pseudogap at $p > p_c$.

The superconducting copper-oxides (cuprates) in the underdoped regime feature unusual states of matter, such as a pseudogap (PG), density-wave order (stripes), and the coexistence of magnetism and superconductivity. Debates regarding the origin and the precise nature of those phases or related phenomena like a reconstruction of the Fermi surface at a quantum critical point are still ongoing actively [1–3]. In particular, interest in the underdoped $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO_y) has been revived in recent years, during which significant progress in understanding those subjects has been made through experimental observations of an electric liquid crystal (ELC) or nematic phase [4, 5], quantum oscillations above a critical doping [6–8], and field-induced charge stripe order [9, 10].

Motivated by the recent literature and by the available high-quality single crystals of underdoped YBCO_y , we carried out a ^{63}Cu NMR study of YBCO_y to elucidate the underlying physics in the highly underdoped region of the compound on a microscopic level. While nuclear magnetic resonance (NMR) is a powerful local probe, so far, the majority of the NMR studies on the planar Cu in YBCO_y has been performed on nearly optimal or slightly underdoped regions [11, 12], largely due to strong magnetism which causes complicated static and dynamic effects on NMR parameters. In this Letter, we show that a critical hole doping p_c exists in the p - T phase diagram of YBCO_y beneath the superconducting (SC) dome at $p \sim 0.1$, below which a static order sets in and above which a spin pseudogap (PG) opens up in the low-energy spin excitation spectrum.

The growth and characterization of detwinned YBCO_y single crystals are described in Refs. [13, 14]. The single crystals investigated here have $y = 6.35$ ($T_c = 10$ K, $p = 0.062$), 6.4 ($T_c = 21$ K, $p = 0.075$), 6.45 ($T_c = 35$ K, $p = 0.082$), 6.5 (sample 1 with short ortho II correlation length [34]: $T_c = 53$ K, $p = 0.106$; sample 2 with long correlation length (~ 100 Å): $T_c = 61$ K, $p = 0.114$), and 6.6 ($T_c = 61$ K, $p = 0.135$), where p is the hole concentration per planar Cu determined from the c -axis

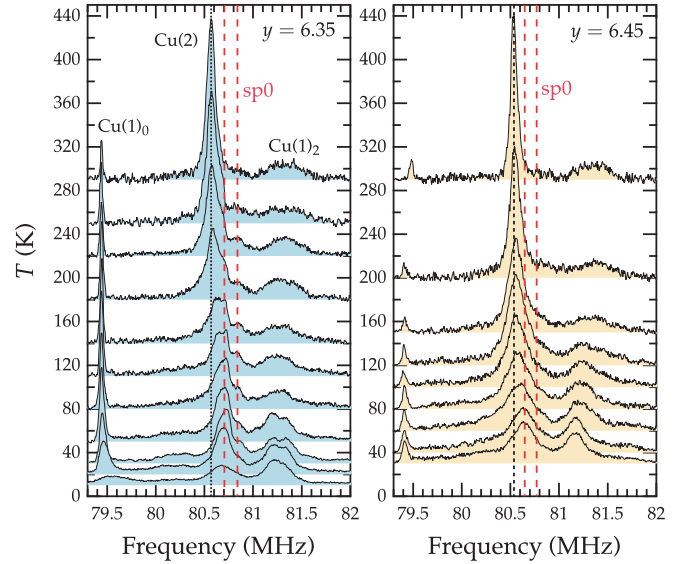


FIG. 1: ^{63}Cu NMR spectra in YBCO_y at 7 T along the c axis for $y = 6.35$ (left panel) and 6.45 (right panel). Cu(1) denotes the Cu sites in the CuO chains, where the subscripts 0 and 2 represent the number of neighboring oxygen ions along the chain, and Cu(2) (dotted lines) denotes the planar Cu sites [16]. An emerging new Cu spectral feature sp0 consisting of two resonance lines indicated by two dashed lines is clearly visible for $y = 6.35$. The horizontal bar indicates the region that was irradiated during a T_1 measurement. See supplementary material for details and for other doping levels [14].

lattice constant [15]. ^{63}Cu NMR spectra were obtained by integrating averaged spin-echo signals as the frequency was swept, and the spin-lattice relaxation rates, T_1^{-1} , were measured by monitoring the recovery of the nuclear magnetization after a saturation pulse.

Fig. 1 shows ^{63}Cu spectra for $y = 6.35$ and 6.45 measured at $H = 7$ T applied along the c axis. The leftmost sharp line and the rightmost broad line in each panel are identified to arise from the Cu(1)₀ and Cu(1)₂ sites,

respectively, in the CuO chains, where the subscript denotes the number of the nearest neighboring oxygen ions *along* the chain [16]. While the central line at room temperature comes from the planar Cu(2) site [16], we find that it evolves in a complicated way as T is lowered, especially for $y = 6.35$ and $y = 6.4$ [14]. The intensity of Cu(2) (dotted line in Fig. 1) is strongly suppressed, and at the same time a new feature sp0, consisting of two resonance lines indicated by two dashed lines emerges at an onset temperature [14]. Clearly, for $y = 6.45$, sp0 occurs at a much lower temperature than for $y = 6.35$. The rapid suppression of Cu(2) with decreasing T is attributed to the *wipe-out effect*, as observed in ^{63}Cu NQR in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_y$ [17], which arises from a slowing down of spin fluctuations [18, 19]. In contrast, the T -dependence of the ^{63}Cu spectra for both $y = 6.5$ and 6.6 are almost identical without any signature of either sp0 or wipeout of Cu(2), except for a moderate broadening with decreasing T [14]. Interestingly, we observed the splitting of the Cu(1)₂ line at low T for $y = 6.35$, which may suggest that sp0 influences Cu(1)₂. In addition, it is noticeable that both sp0 and Cu(1)₀ broaden significantly at low T below 20 K for $y = 6.35$, suggesting the occurrence of glassy or incommensurate magnetic order. Note that such a broadening could not be measured for $y = 6.4$ and 6.45 , because the magnetic order occurs deep in the superconducting state where the NMR spectra significantly weaken and become complicated.

Fig. 2 shows the recovery of the ^{63}Cu nuclear magnetization after a saturating pulse as a function of delay time t at various temperatures for $y = 6.35$ and 6.45 , measured at the Cu(2) line. Unexpectedly, we found a step-like feature in the data, which indicates two T_1 -processes. The long T_1 process becomes discernible at 265 K for $y = 6.35$ and at 120 K for 6.45 , and its fraction (i.e., $1 - m(t)$ at the step) increases rapidly with decreasing T . Comparing with the T -dependence of the spectrum as shown in Fig. 1, we find that the long $T_{1\ell}$ component arises when the new spectrum sp0 becomes visible, suggesting that sp0 is due to an emerging static phase featured by the long $T_{1\ell}$ [14]. Since two T_1 processes are evident in the relaxation data, we used a fitting function for magnetic relaxation of the central transition for $I = 3/2$ including two T_1 components,

$$m(t) = \left[1 - a \left\{ (1 - w) \left(0.1e^{-t/T_{1s}} + 0.9e^{-6t/T_{1s}} \right) + w \left(0.1e^{-t/T_{1\ell}} + 0.9e^{-6t/T_{1\ell}} \right) \right\} \right], \quad (1)$$

where a is a fitting parameter which is ideally one for saturation recovery. T_{1s} ($T_{1\ell}$) are the short (long) T_1 components, and w is the fraction of the volume governed by the long $T_{1\ell}$ process to the total volume. Solid curves in Fig. 2 are fits to Eq. (1). At low T (≤ 70 K), it was necessary to impose the stretching exponent β in Eq. (1) for the $T_{1\ell}$ recovery, which is indicative of a crossover to

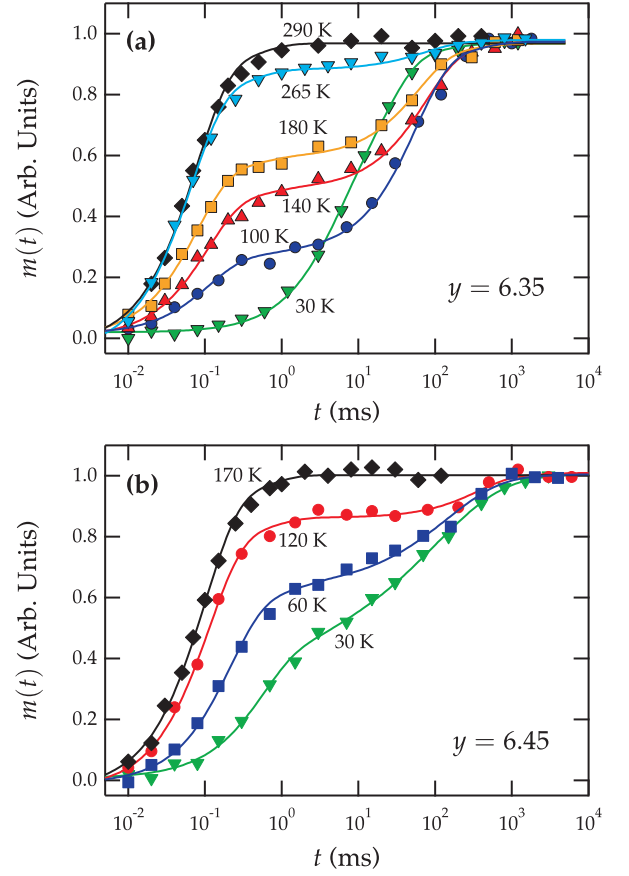


FIG. 2: Recovery of the (normalized) nuclear magnetization $m(t)$ as a function of time t for $y = 6.35$ (a) and $y = 6.45$ (b). In (a), $m(t)$ deviates progressively from a single T_1 -process with decreasing T , revealing the long $T_{1\ell}$ -process which overwhelms the short one at low T . Note that the short T_{1s} -component is no longer detectable at 30 K. In (b), the $T_{1\ell}$ -process is strongly suppressed i.e., it appears below ~ 150 K and a large portion of the T_{1s} -process remains down to 30 K. Solid lines are fits to Eq. (1).

a glassy magnetic phase.

The resulting $(T_{1s}T)^{-1}$, $(T_{1\ell}T)^{-1}$, and w as a function of T and for all y are presented in Fig. 3. The results in $\text{YBCO}_{6.6}$ are compatible with data known so far [16], revealing the spin pseudogap with the onset $T^* \sim 145$ K. The spin-lattice relaxation rate probes the gap solely in the spin excitation spectrum since $(T_1T)^{-1} \propto \sum_{\mathbf{q}} A^2(\mathbf{q})\chi''(\mathbf{q}, \omega_0)$ where $A(\mathbf{q})$ is the hyperfine coupling constant and ω_0 the Larmor frequency. Therefore, the onset temperature of the PG and its doping dependence obtained by $(T_1T)^{-1}$ can be significantly different from those obtained by the Knight shift, which probes the spin response at $\mathbf{q} = 0$ only [17], and other techniques such as ARPES and optical conductivity which probe the charge gap [1]. For $\text{YBCO}_{6.5}$, T^* is reduced to ~ 110 K as indicated by arrows. We performed the measurement in another $\text{YBCO}_{6.5}$ crystal which has a longer ortho-II correlation length ~ 100 Å. For this

sample, both p and T_c turns out to be larger than the sample with shorter correlation length, being consistent with slightly larger T^* . Upon further lowering y to 6.45, $(T_{1\ell}T)^{-1}$ increases with decreasing T reaching a plateau below ~ 150 K, which is in contrast to the pseudogap behavior reported in a similarly doped compound [20]. $(T_{1s}T)^{-1}$ of YBCO_{6.35} and YBCO_{6.4} is further enhanced with no signature of the PG as well, although T_{1s} is not measurable below 100 K and 50 K, respectively, due to limited experimental resolution [see Fig. 2(a)]. Note that the T -dependence of the data undergoes a dramatic change as y is reduced from 6.5 to 6.45, implying the existence of a critical doping just below $y = 6.5$.

Fig. 3(b) shows the long relaxation rate $(T_{1\ell}T)^{-1}$ versus T which arises from the sp0 line. For comparison, corresponding $(T_{1s}T)^{-1}$ data of Cu(2) are also shown. ($T_{1\ell}$ is not detected for $y = 6.5$ and 6.6.) In YBCO_{6.35}, $(T_{1\ell}T)^{-1}$ is almost constant at high T , but it starts to rise steeply below ~ 100 K, forming a sharp peak centered at ~ 11 K. These behaviors, together with the significant broadening of the spectra at low T , lead to the conclusion that a spin freezing or spin-glass (SG) transition occurs at a characteristic temperature $T_g \sim 11$ K for $y = 6.35$. We find that our data resembles the results of ^{89}Y NMR in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ [17] and ^{139}La NQR/NMR in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [21, 22]. Similar T -dependencies of $(T_{1\ell}T)^{-1}$ were also observed for $y = 6.4$ and 6.45. Although we were not able to identify the local maximum for these doping levels due to the higher T_c which complicates the identification of T_g by NMR, one can obtain $T_g \sim 5$ K for $y = 6.45$ from the μSR study of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_6$ which shows a very similar p -dependence of T_g [23].

Fig. 3(c) shows the volume fraction w as a function of T , obtained from the fit of relaxation data $m(t)$ using Eq. (1). It should be emphasized that the values of w themselves have no quantitative meaning, since they may depend on the frequency at which the relaxation rates were measured. Moreover, the wipeout of Cu(2) should lead to a significant increase of w , particularly at low T , which is indeed thought to account for the rapid increase of w at low temperatures [see Fig. 3(c)]. Nonetheless, the temperature at which $w \rightarrow 0$, i.e., where the $T_{1\ell}$ process vanishes with increasing T should be unaffected by those facts. Thus, with reasonable accuracy, one can define the onset temperature T_0 from the values extrapolated to $w = 0$, denoted by arrows.

From these results, we draw the p - T phase diagram in Fig. 4. The most striking feature is that T_0 falls rapidly to zero at a hole concentration of $p \sim 0.1$ beneath the SC dome. At the same time, the SG transition temperature T_g shows also similar doping dependence, being terminated at p where $T_0 \rightarrow 0$. These behaviors suggest a close relationship between T_0 and T_g , collapsing to the same critical doping $p_c \sim 0.1$. Interestingly, it turns out that p_c is very near the doping level at which the metal-

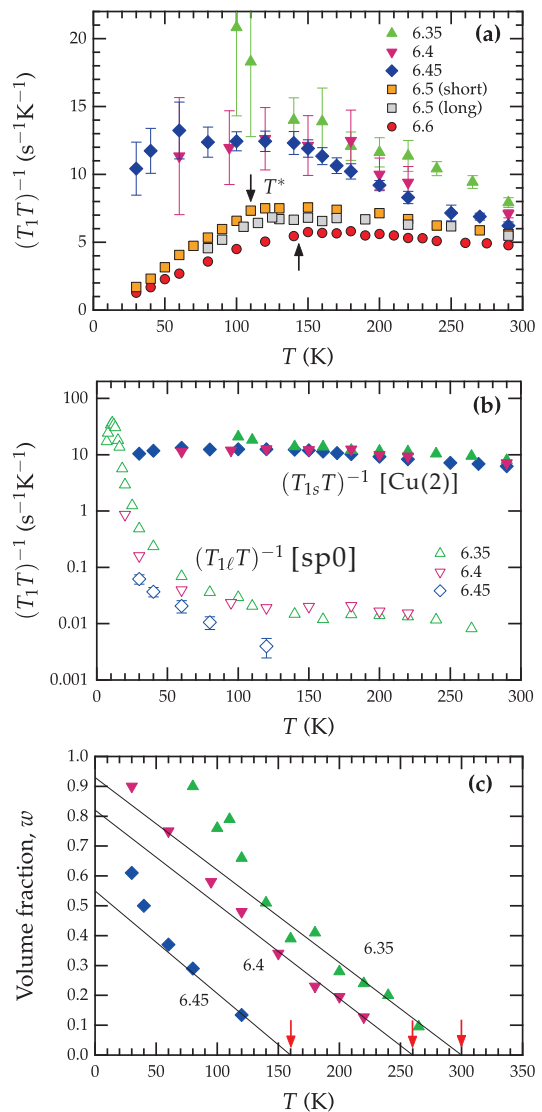


FIG. 3: (a) Nuclear spin-lattice relaxation rates divided by T , $(T_1T)^{-1}$ versus T for the short T_{1s} . The opening of the PG at T^* (denoted by arrows) was detected only for $y \geq 6.5$, whereas there are no signatures of the PG for $y \leq 6.45$. In (b), $(T_{1\ell}T)^{-1}$ data are presented, together with $(T_{1s}T)^{-1}$ for comparison. In YBCO_{6.35}, $(T_{1\ell}T)^{-1}$ forms a local maximum at $T_g \sim 11$ K, indicating a SG transition. This behavior is significantly suppressed for $y = 6.45$. (c) T -dependence of the volume fraction w . The onset temperature T_0 is defined from the values at which $w \rightarrow 0$ (down arrows).

insulator crossover (MIC) takes place [24] or the Fermi surface is reconstructed by density-wave order [8, 9, 25]. The phase diagram is also in qualitative agreement with that suggested by inelastic neutron scattering (INS) and muon spin rotation (μSR) studies [13, 26].

A remarkable finding in our study is that the *spin* pseudogap is observed only near and above p_c (i.e., $y \geq 6.5$) [see Figs. 3(a) and 4]. Note that T^* of YBCO_{6.5} positioned near p_c is much lower than the value expected

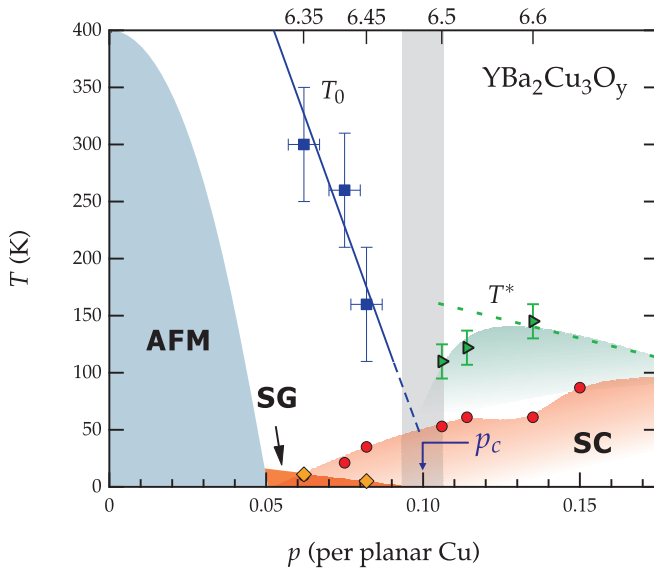


FIG. 4: Phase diagram of underdoped YBCO_y in terms of hole concentration p . y values are shown on the top axis for convenience. AFM transition is from Ref. [13] and dotted line drawn for T^* is estimated from previously known NMR results [11, 17].

based on extrapolation of the doping dependence established at higher p , which is indicated by the dotted line. Indeed, the sudden drop of T^* near p_c in YBCO_{6.5} appears as a crossover to the absence of T^* in YBCO_{6.45}, corroborating the INS results in which the suppression of the low energy spin excitations (i.e., spin pseudogap) was not detected down to 5 K in YBCO_{6.45} [5, 27, 28]. Such an abrupt suppression of the spin pseudogap *below a critical doping level* was reported in NMR studies not only of similarly hole-doped Y_{1-z}Ca_zBa₂Cu₃O_y [17] but also of the multi-layer cuprate Ba₂Ca₂Cu₃O₆(F_yO_{1-y})₂ [29]. By the same token, the fact that p_c is in the vicinity of the MIC [24] agrees well with the disappearance of the quantum oscillations below $\sim p_c$, as well as with the NMR result in Bi₂Sr_{2-x}La_xCuO_{6+δ} that the ground state of the PG is metallic [30]. Therefore, we argue that the spin PG phenomenon may be quantum critical, stemming from the suppression of magnetism. In fact, such a strong competition between magnetism and the PG gives a good account of the observation that the PG is abruptly suppressed by substituting the Cu(2) sites with $\sim 1\%$ Zn impurities around which a local moment is induced on the Cu(2) sites in YBCO_{6.7} [31] and YBa₂Cu₄O₈ [32].

While the nature of static order which appears at T_0 is unclear yet, one may consider T_0 as the onset of stripe-like charge modulation in the plane, possibly induced by the end Cu ion of the oxygen-filled chains, Cu(1)₁. In fact, as effective impurities, Cu(1)₁ sites can cause Friedel-like oscillations [33], which may in turn induce the stripe-like charge modulation in the plane. This would be consistent with a higher T_0 at lower p , where the num-

ber of Cu(1)₁ is higher. The charge modulation scenario agrees well with signatures of broken rotational symmetry observed in resistivity [4] and INS [5, 13] measurements at $p < p_c$. In this case, the planar Cu(2) sites should be differentiated into two spatially modulated distinct regions. In terms of stripes, the short T_{1s} -yielding region is naturally related to spin stripes which consist of the localized Cu(2) spins, while charge stripes may yield the long $T_{1\ell}$ if the spin contributions to the relaxation rates were almost quenched. Although the stripe-like charge modulation accounts for our results to large extent, it remains a question whether the two alternating regions in the stripe structure could, in practice, result in the $(T_{1s}T)^{-1}$ and $(T_{1\ell}T)^{-1}$ values that strikingly differ up to three orders of magnitude.

In summary, we performed a systematic ⁶³Cu NMR study as a function of doping and temperature in highly underdoped YBa₂Cu₃O_y, showing that static order, probably stripe-like, emerges at the onset temperature T_0 , being followed by glassy magnetic order at T_g . The resulting phase diagram includes a critical hole doping $p_c \sim 0.1$, at which both T_0 and T_g fall to zero. Another important finding is that the spin pseudogap was detected only above p_c , suggesting that the spin pseudogap phase competes with the magnetic order and/or the static order detected at T_g and T_0 , respectively.

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